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FLOCCULATION AND SEDIMENTATION OF DISPERSED PARTICULATE SYSTEMS: RECENT DEVELOPMENTS*

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ABSTRACT

The properties and characteristics of discharged tailings material can be traced, not only to the source material variations, but also to the many complex processes brought to bear, from conditioning, digestion, and separation stages in the extraction of product material. The complex interactions established between the various constituents in the tailings material discharged, can be evaluated in terms of specific suspension volumes -- which express the amount of water held by each specific constituent in the tailings. Furthermore, the subsequent dynamics of the material -- settling, dehydration and crusting -- can be better assessed if the mechanisms which promote interaction between the constituents are better understood. The suspension volume concept provides the first step towards this direction.

INTRODUCTION

The basic compositional constituents for dispersed particulate systems, produced as a result of mineral extraction processes from host rock, can be broadly grouped into 4 groups.

These are:

(a) inorganic solids consisting primarily of mineral particles and amorphous materials,
(b) organics and humic material,
(c) dissolved and undissolved electrolytes, and
(d) micro-organisms.

The general terms used to identify these dispersed particulate systems include: tailings material, slurries, slimes, and sludges. By and large we can consider slurries to contain groups (a) and (c). Slimes are akin to slurries and may contain group (d). Sludges contain groups (a) through (d). Note that there will always be exceptions to the general rule. However, by and large, the basic compositional constituents in slurries, slimes and sludges described above are well established. Note that groups (a) and (c) are common to slurries, slimes and sludges. In many instances, specialized terms are also used: e.g. red mud, phosphatic clays, etc. However, the basic problems pertaining to a general dispersed particulate system remain as common issues, i.e. poor settling characteristics of the slurries and high containment requirements. Figures 1 and 2 demonstrate the problem at hand. The idealization shown in Figure 2 is meant to portray the commonly found stagnant zone where the solids concentration for many slurries appear to hover -- between 30 to 50% solids concentration. This idealized profile is thought to be more representative of Section III in Figure 1, where shoreline discharge of tailings occurs in practice.

STABILITY OF SUSPENDED MATERIAL

In the context of the present discussion on dispersed particulate systems, the presence of groups (a) and (c) are necessary and sufficient conditions for development of the

dispersion stability of suspensions. The addition of groups (b) and (d) serve to both reinforce the dispersion stability of the suspended solids and to alter the complex interactions occurring within the suspension. Common experience with tailings waste containment ponds testify to the problem of reluctant gravitational settling of the suspended solids in the ponds, e.g. Yong et al, (1983), Bureau of Mines, (1975). Since all these waste discharge tails are suspensions, the general term SUSPENSION will be used whenever convenient - to facilitate discussion.

At least three mechanisms can be postulated as being contributing mechanisms for the dispersion stability of suspensions consisting of surface active solids, such as those found in SUSPENSIONS. These are: (1) mutual repulsion of solids due to high zeta potential, (2) adsorption or coating of amorphous material (small lyophilic colloid) on a large electronegative colloid; [the affinity of amorphous material for water exceeds the net attraction of the van der Waals forces], and (3) steric hindrance due to adsorption of an oriented non-ionic organic molecular layer.

In a suspension containing various kinds of constituent solids, we expect all three mechanisms to be present - with differing degrees of influence - in the promotion of the dispersion stability of the suspension. It would be correct to note that it is indeed likely that other mechanisms may exist as complex variants of the above three mechanisms. However, these have yet to be fully identified and documented.

Flocculation and Coagulation

Since solids-liquid self-weight separation will involve processes which have been identified or defined as flocculation and coagulation, it is necessary to define the these terms. The

terms "FLOCCULATION" and "COAGULATION" have often been misused interchangeably - even though each identifies a separate resultant interaction process.

FLOCCULATION as defined by La Mer, is the destabilization of suspensions with the use of natural or synthetic polymers which absorb onto the particles in the suspensions, thus forming bridges between particles and causing aggregation or agglomeration of large assemblies of particles. These agglomerates can only be dispersed into smaller particle groups through the use of mechanical or physical disruptive shear forces.

COAGULATION refers to the destabilization of suspensions by a reduction of the electrostatic repulsive forces, thus allowing the van der Waals attraction forces to cause particle aggregation. The aggregate groups formed can be reversibly dispersed only if secondary bonding, such as cementation bonding between particles, does not occur as a result of biological-/chemical reactions in the ageing period.

The term FLOCS has been used very loosely to describe the agglomeration of particles resulting from the "flocculation" process. This is obviously incorrect since flocs can also be formed through coagulation. FLOCS refers to the grouping (agglomeration, aggregation or clustering) of particles in a manner such that the particles are arranged in a "card-house" structure, i.e. the particles are arranged in an edge-to-edge and edge-to-face configuration. The production of flocs can occur through flocculation or coagulation processes. HOWEVER, it is important to distinguish between flocculation-generated-flocs and coagulation-generated-flocs since the STABILITY OF THE FLOCS will be different. As noted above in the definition of flocculation and coagulation, the flocs generated through coagulation can be reversibly dispersed whilst the flocs developed through flocculation will require mechanical or physical energy input to

destabilize the flocs. It would indeed be simpler to use different terms for the two kinds of flocs. However, common usage of the term in the context of a "card-house" structure permits us to continue usage of the term SO LONG AS we pay particular attention to source mechanisms for the generation of the flocs.

In suspensions (i.e. dispersed particulate systems) consisting of lyophobic colloids, such as slimes, slurries, sludges, red muds, phosphatic clays, etc, it is recognized that their stability depends on the characteristics of particle interaction. The quantitative theory of stability of lyphobic colloids, identified as the DLVO theory (after Derjaguin, Landau, Verwey and Overbeek), which constructs its analytical model on the basis of (a) electrostatic repulsive forces due to interpenetration of the diffuse ionic layers, and (b) van der Waals attraction forces, provides us with a basis for calculation of the energies of interaction between the suspended solids.

Net repulsion occurs between particles (colloids) when double layer repulsion overwhelms van der Waals attraction. The presence of potential determining anions such as bicarbonates, carbonates, hydroxides, phosphates, etc. in the fluid phase, all contribute to the enhancement of net repulsion.

When attractive forces dominate, the system becomes unstable and coagulation occurs. At least two factors are important in the coagulation process: (a) Brownian motion of the constituents particles, and (b) particle interaction. In a system where the repulsive forces are vanishingly small and can be neglected, Brownian collision between particles will lead to agglomeration or aggregation of the particles - thus leading to the production of floc units. Note however that not every collision will result in aggregation. For two different systems, given the same collision frequency, the effectiveness of

aggregation upon collision depends on the properties of the particle surfaces. Under such circumstances, this kind of phenomenom is identified as "slow coagulation".

When the rate of aggregation upon collision does not depend on the properties of surfaces, and is conditioned only by the collision frequency, the process can be identified as "fast coagulation" . The process of coagulation which is caused by the addition of electrolytes, demonstrates the role of the electric state of the interface in the following fashion: (a) coagulation is induced by the ions of charge opposite to that of the particles, (b) similar values of zeta potential will yield correspondingly similar rates of coagulation, and (c) the valency of the ion involved is influential in the determination of coagulation power.

In clay mineral suspensions, the zeta potential at any given clay:water ratio depends on the concentration of electrolyte in the suspension. The mono-molecular layer of the electrolyte on the clay surface is formed at a particular concentration. Yong and Sethi (1977) have shown that a strong relationship exists between the dispersion stability (of the suspension) and the zeta potential of the system, (Table 1).

Table 1 - Dispersion stability of clays and zeta potential

Stability characteristics	ave. zeta potential, mv.
1. Maximum agglomeration and precipitation	+3 to 0
2. Excellent agglomeration and precipitation	-1 to -4
3. Fair agglomeration and precipitation	-5 to -10
4. Threshold of agglomeration	-11 to -20
5. Plateau of slight stability (few domains)	-21 to -30
6. Moderate stability (no domains)	-31 to -40
7. Good stability, i.e. stable suspension	-41 to -50
8. Very good stability	-51 to -60
9. Excellent stability	-61 to -80
10. Maximum stability	-81 to -100

In the ongoing study of the dispersion stability of clay slimes generated from the spearation processes of weathered soil for extraction of coarse aggregate, (in Singapore), the zeta potential of the samples obtained in the stagnant zone show values ranging from -35 to -57 mv. These values, which fit into categories 7 and 8 in Table 1 (good to very good stable suspensions), confirm visual and experimental experience with the recalcitrant settling characteristics of these slimes, (solids concentration of about 37%).

Dispersions of lyophobic colloids (surface active solids) in suspensions are stable due to the presence of strong mutual repulsive forces. Agglomeration or flocculation can be achieved many ways:

1. Through lowering of the zeta potential of the system to zero with the use of a strong cationic electrolyte.
2. Through the use of a strong cationic electroylyte in conjunction with an appropriate alkali. Optimum pH is required.
3. By adding a reagent which results in the formation of an insoluble matrix which engulfs and binds the water in the system. Subsequent removal of the water may be accomplished through such methods as consolidation or electro-osmosis, etc.
4. Agglomeration through the addition of sufficient cationic polyelectrolytes and with recovery of the water through filtration or centrifugation.
5. Agglomeration with long chain or branched-chain anionic polyelectrolytes.
6. Agglomeration with non-ionic long chain or branched-chain polymers.

In suspensions with clay minerals and other soil constituents, the protective coating of amorphous material on clay surfaces may result in strong repulsion between particles, thus rendering stable dispersion conditions. By and large, we note that the amorphous material is composed of oxides of silica and oxides and hydrous-oxides of alumina, and iron. Amorphous materials with high net negative charge and high SiO_2/Fe_2O_3 ratios are generally obtained through chemisorption of silica on ferric hydroxide. Experience has shown that they have a strong affinity with water, and that their properties change on drying. Recent studies in our laboratories show that amorphous materials tend to coat the primary minerals, and to a much lesser extent, the clay minerals. Note that a positively charged amorphous iron-silicate-hydroxide can also be obtained under different environmental conditions. Such a condition for example would be when silanol groups of polysilicic acid react with basic metal groups.

Non-ionic organic molecules are not adsorbed in measureable amounts from aqueous solutions unless there are more than six carbon atoms in the molecule. However, in a non-aqueous environment, their vapours are adsorbed in lesser amounts. Most of the work done in this kind of problem has been in regard to hydroxylic compounds which are adsorbed by hydrogen bonding of polar active groups to oxygen rich clay surfaces. Multiple dispersion forces associated with the many surfaces, contacts per molecule, and the entropy factor are the most important factors contributing to the adsorption of these large molecules. Other important considerations are configuration, moleculer weight and chain length of the organic molecules.

SETTLING/SEDIMENTATION PROCESS

A way in which one can describe the solids-liquid self-weight separation process is to study the settling/sedimentation and consolidation process. This is performed by tracing the "life" or status of a typical representative solid, beginning with its initial state. When discharged, and after formation of a beach, the solids in the slurry in Section III in Figure 1, will settle in a fashion more or less controlled by either gravitational forces or by interactive forces dictated by brownian collision, or by surface-active relationships. The settling process in Section II, Figure 1, is also driven by forces associated with the discharge procedure. Turning our attention to Section III, it is expected that since the concentration of solids concentration in this region (shown as the top two layers in Figure 2) is not sufficient to account for proximal hindrances, one might apply lessons from gas dynamics and seek to promote analyses of suspension stability using binary collision theory, such as that reported by Yong and Wagh, (1985). When surface active forces begin to overpower simple brownian motion, calculations of the settling rate of the suspended solids

must be performed with full accounting for the energies of interaction between solids. The ideal theories, e.g. DLVO, of particle interaction can be invoked to provide one with a sense of the dispersion stability of the suspension.

When settling of a representative solid progresses to the stage where neighbouring solids begin to interfere, the tediously slow settling performance of the solids is apparently hindered not only by the physical interferences of neighbouring solids, but also by interactions controlled by surface active relationships. Because the settling process of suspended solids is a continuous process, the separation between various mechanisms which begin to fully dominate settling characteristics will never be easily defined. At some point, the hindered settling performance will lead to the development of effective stresses, i.e. pore water pressures will be developed. At this time, large strain consolidation modelling can be satisfactorily can be performed -- as shown by Yong et al, (1984) and Yong and Ludwig (1985).

THE CONCEPT OF SUSPENSION VOLUMES

The dispersion stability of the solids suspension, which is indicative of the degree to which the solids remain in suspension, is a direct result of the water-holding capability of the solids. From concepts of diffuse-double layer interaction, it is known that the maximum amount (volume) of water held by each solid or floc is obtained when the counter-balancing ions in the surrounding fluid neutralize the surface charge requirements of the active solid or floc. When two or more solids/flocs interact, this situation is characterized by a zero midplane potential. This can be pictorially represented by the single particle shown in Figure 3, where the counter-ions are shown surrounding a charged plate, and in Figure 4, where the water shell equivalent is depicted. The thickness of this shell, or

the volume of water, can be computed from theoretical considerations using the DLVO model (Yong, 1984). When two or more solids/flocs interact, this situation is characterized by a zero midplane potential -- as seen in Figure 5 where an ideal three-particle parallel arrangement is shown. The amount of water held in this system can be defined as the equilibrium suspension volumem, specific to the solid under consideration and for a zero midplane potential situation. The term "equilibrium suspension volume" thus implicitly denotes a zero osmotic pressure condition. Whilst energy-separation distance calculations will give the most likely equilibrium interparticle spacing and void ratio of the system, representative of the zero osmotic pressure condition, it must be recognized that real slurry systems depart from idealization due to: (a) floc formations, (b) mixed aggregative systems, and (c) presence of other kinds of constituents.

In recognition of the real system, one can approach the calculation of equilibrium water volumes associated with the specific constituents by considering the following thesis: If each solid, or floc "holds" onto a specific volume of water as its "equilibrium" shell of water (defined as the specific suspension volume), consistent with the balance of internal and external energies, the total stable dispersed state of the suspended solids at a particular depth in the containment pond, will show that the total volume of water retained in a representative unit volume would be equal to the sum of the specific suspension volumes, i.e. equal to the sum of the volumes of equilibrium water held by the individual component solids. A simple pictorial representation of this thesis is shown in Figure 6. The various "starbursts" and crossed-circles shown in the Figure are meant to represent the constituents with their equilibrium suspension water volumes. Obviously, the other spaces not shown with constituents will also contain other specific suspension volumes. Yong and Sethi (1978) have shown

from controlled laboratory experiments with mono-mineralic clay suspensions, that the measured equilibrium suspension volume of water associated with specific minerals at zero osmotic pressure, (Table 2), show good correspondence with those computed using the theoretical interaction model, - provided that the theoretical calculations account for the presence of the potential determining anions. The extreme right hand column of Table 2, shows the experimental methods used for determination of the specific suspension volumes. The use of measured suspension volumes in calculating field values of pond suspension volumes, releases one from prior assumptions concerning floc formation or preferred orientations, and will account for suspension fluid chemistry if the same chemistry is used in the experimental tests.

It is useful to note that for suspensions under measurable solids self-weight and even under external stressing conditions, the concept of suspension volumes can be readily applied. If the stresses are calculable, the internal stresses generated between particles -- as interparticle forces or energies of interaction -- can be calculated by considerations of balance of internal and external energies. The equilibrium stress balance situation (between external and internal) will produce equivalent suspension volumes for individual constituents, and can be expressed as "stress-equilibrium suspension volumes". This aspect of the suspension volume concept is particular useful in considerations of large-strain consolidation. Taken to its other end of the spectrum, i.e. in natural soils, the soil-water energy characteristic is a particular application of this concept.

In the following example, taken from Yong (1984), the suspension volumes reported in Table 2 have been used to calculate the "expected" solids concentration in a tin mining slime pond. The constituents in the slime, and their

proportions, which were determined in laboratory analyses, are reported in the first column. The second column shows the measured suspension volumes associated with each type of mineral, (from Table 2), and the third column shows the volume of water associated with each constituent in a 100 gram sample.

Mineral	Suspension Volume, cc/gram (from Table 2)	Specific Volume in Sample, cc/100 gms.
kaolinite - 45%	1.3	58.5
mica - 10%	3.0	30.0
gibbsite - 2%	1.0	2.0
quartz - 40%	0.14	5.6
other - 3%	0.15	0.45
Total = 100% (or 100 grams of solids)		96.55

Hence, weight of water = 96.55 grams.

Total weight = (100 gms. solids) + (96.55 gms. water)
= 196.55 gms.

Computed solids concentration = 100/196.55 = 50.8%
Measured solids concentration = 52%

The comparison between measured and computed solids concentration appears to agree very closely. Table 3, (from Yong, 1984) shows the comparison between "predicted" and measured solids concentration values for various types of waste slurry containment ponds studied. Since the "fine-tuning" of the concept was performed and calibrated with the tar sand sludge ponds, it is not surprising that the agreement between "predicted" and measured values is indeed excellent. However, application to other types of ponds shows clearly that the suspension volume concept is not only viable, but applicable.

Table 2 - Suspension volume for various minerals and method of their determination

Sample No.	Mineral	Suspension Volume (cc/g)	Void Ratio	Specific Gravity	Method of Determination
1	Kaolinite	1.3	3.44	2.65	Settling of pure kaolinite in $NaHCO_3$ for 18 months.
2	Illite	3.1	8.15	2.65	Settling of kaolinite: illite (40:60) in $NaHCO_3$ for 18 months.
3	Montmorillonite	21.5	57.0	2.65	Settling of Na-montmorillonite for 36 months.
4	Amorphous Fe_2O_3	20.5	82.0	4.00	Settling of Fe_2O_3+ kaolinite: illite in $NaHCO_3$ for 18 months, containing 4.5% Fe_2O_3.
5	Gibbsite	1.0	2.65	2.65	Estimated from kaolinite experiments.
6	Mica	3.0	7.95	2.65	Estimated from illite experiments.
7	Quartz	0.14	0.37	2.65	Estimated from Theory of Mixtures.
8	Others*	0.42	1.12	2.65	Assumed.

*Includes feldspar, calcite, ankerite, siderite and pyrite.

Table 3 - Comparison of theoretically computed and measured solids concentration (S.C.) for samples studied

Source	Theoretical S.C. %	Measured S.C. %	Theo. S.C. / Meas. S.C. %
Phosphatic Slime	13.4	14	0.96
Aggregate Slime	10.5	14.3	0.71
Tin Mining Slime	50.8	52	0.98
Clay Coating Slurry	51.8	52.7	0.93
Beneficiation Slurry	9.1	8.7	1.05
Tar Sands Sludge	42.2	41.9	1.01
Bauxite Red Mud	Not computed	20-40	
Soil-Organic Slime	Not computed	2-19	

It is necessary to note that both the theoretically computed and measured values must be considered as "average representative" values since: (a) the method used for determination of the proportion of various minerals from x-ray diffractograms, (b) sampling procedures, (c) quality of samples and how well they represent the actual conditions of the material in the ponds, are significant considerations.

PROCESSING AND SLIME/SLUDGE PROPERTIES

The connection between processing parameters and procedures, and properties, characteristics, and subsequent behaviour of the discharged slime/sludge (tailings) has not been generally established. It seems highly likely that a definite link between two must exist -- since processing, separation, and extraction procedures require that the source material be thermally, physically, and chemically manipulated. In a simplistic way, we presume that mechanical/physical actions, additives and water/heat added at the conditioning and digestion stages, to facilitate processing, will result in transformation and alterations in the constituents which "are left behind" as material for discharge. The somewhat counter-opposing additive functions at the digestion and separation stages, can only add to the complex chemistry of interaction between constituents in the final tailings discharge material. In simple terms, the additives and actions provided in the digestion stage serve to provide a certain degree of dispersion of the fines, to facilitate processing. At the separation stage, one tries to settle the suspended solids quickly and efficiently, and to provide for a high quality liquor or froth -- to yield efficient extraction of the product material. The sediment discharge in the separation stage should be as compact as possible, (and yet demonstrate good dewatering capability), in order that no undue loss of liquor or froth occurs in the sediment.

The result of all the above actions can only serve to influence the developed suspension volumes of the individual constituents, and the overall suspension volume. It is not immediately clear that the dispersion stability of the suspension is not tied intimately with all the intricate processes which begin at the conditioning stage. Furthermore, subsequent tailings discharge performance will also be affected, e.g. settling, dewatering, drying and dehydration, crusting, bonding and irreversibility of bond formation, stability of crusts or dehydration layer, stability of sedimented/consolidated layers, dust formation, etc. Since all the properties and behaviour of the material are derived from interactions between the constituents, and since these can be categorized by the specific suspension volumes, the consideration developed in the earlier part of this paper, concerning suspension volumes becomes significant.

CONCLUDING REMARKS

The status of tailings in a containment pond can be traced to the complex processes brought to bear, from conditioning through digestion, and through separation processes. The complex interactions established between the various constituents in the tailings material discharged can be evaluated in terms of the specific suspension volumes -- which expresses the amount of water held by each specific constituent. The ability to release the water in the suspension volumes constitutes the central issue, and can be better assessed if the mechanisms are more clearly understood. The concept of suspension volumes is the step towards this end.

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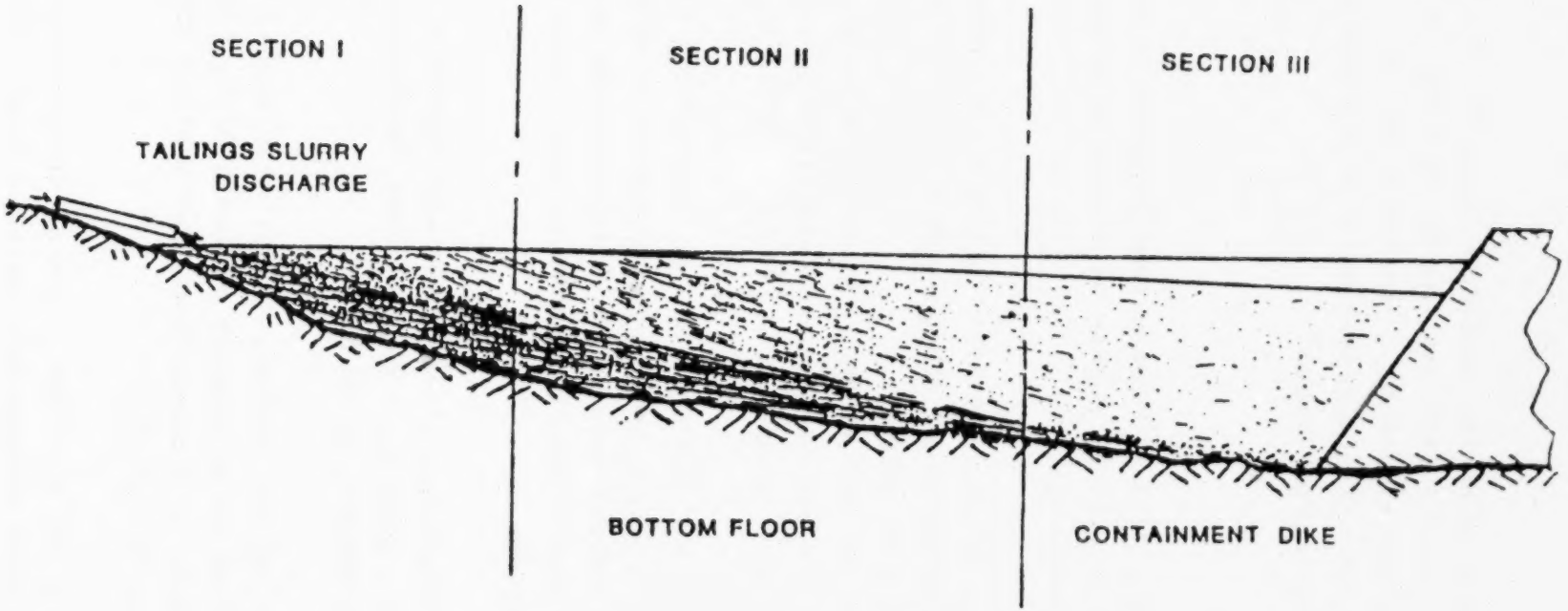


Fig. 1. Schematic view of general waste tailings discharge.

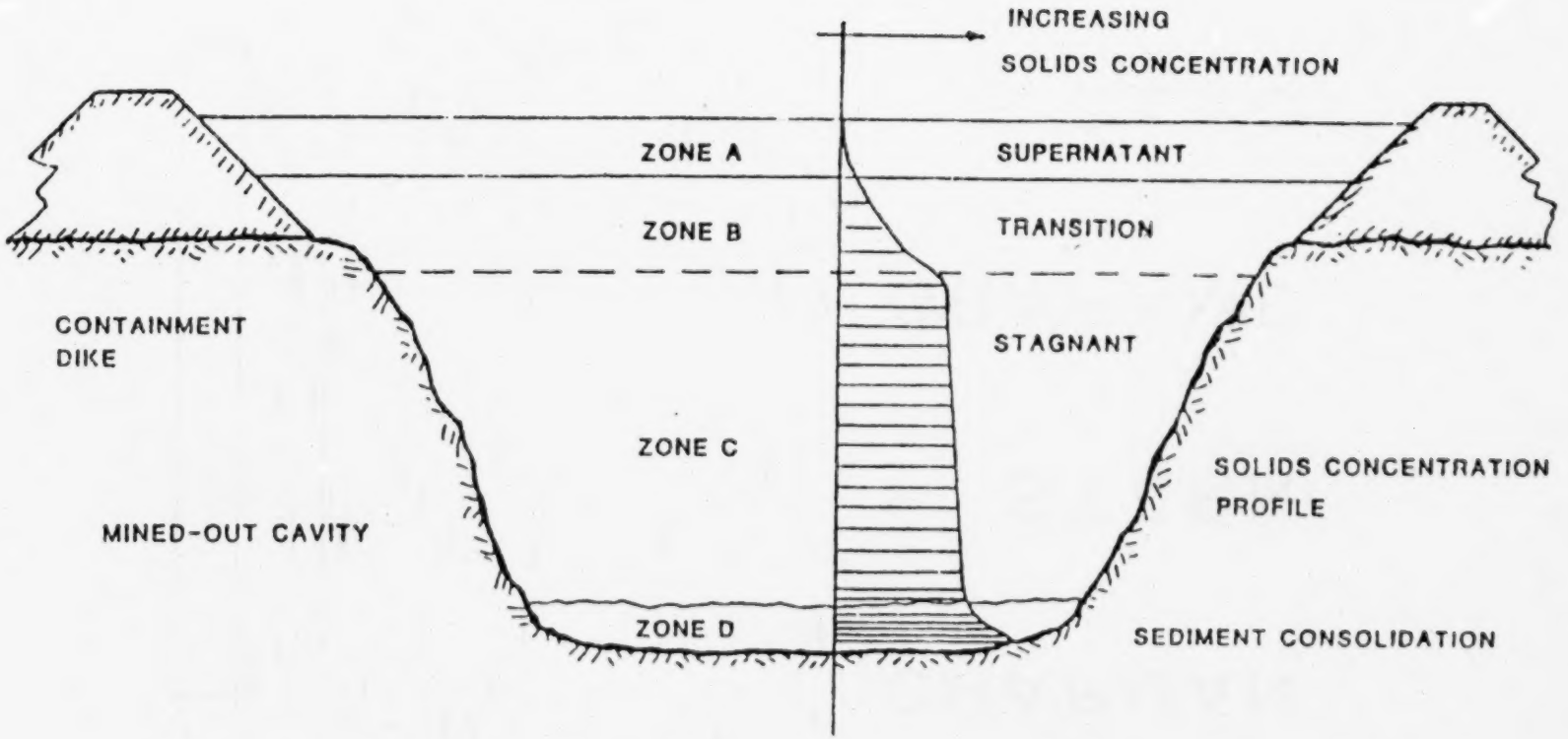


Fig. 2. Idealized schematic of settling pond.

Fig. 3. Counter-balancing ions and charged plates. Note that names refer to analytical models.

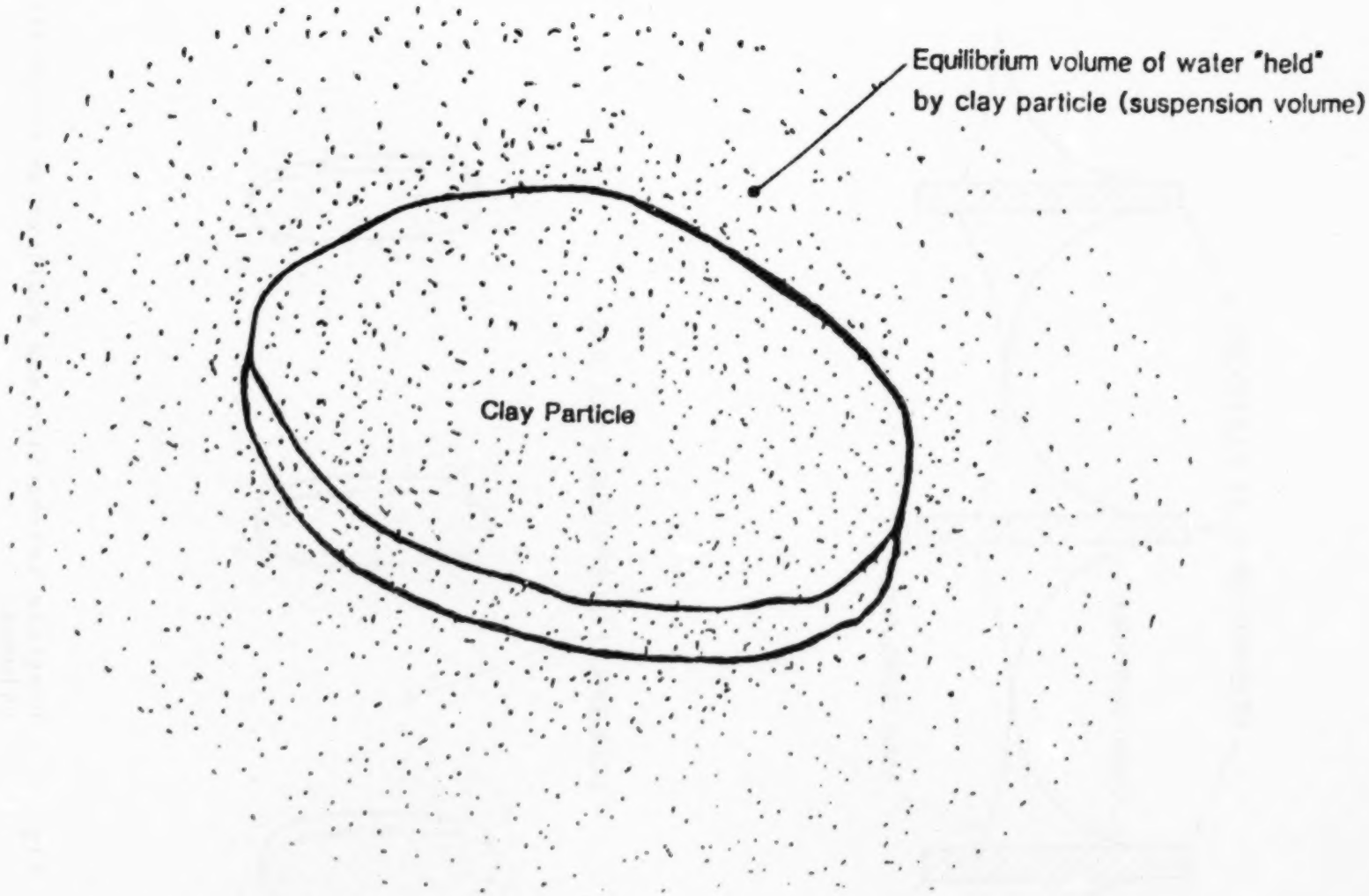
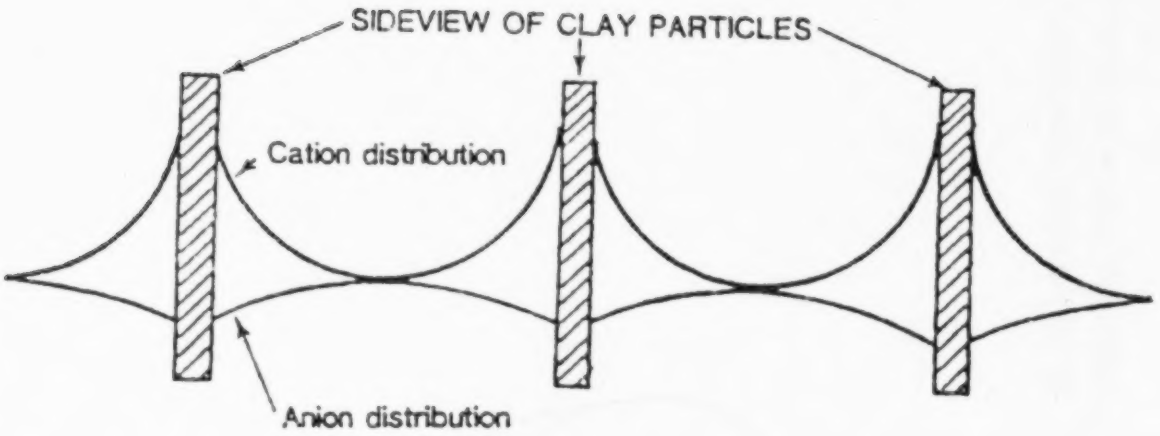


Fig. 4. Simple clay particle suspension volume.



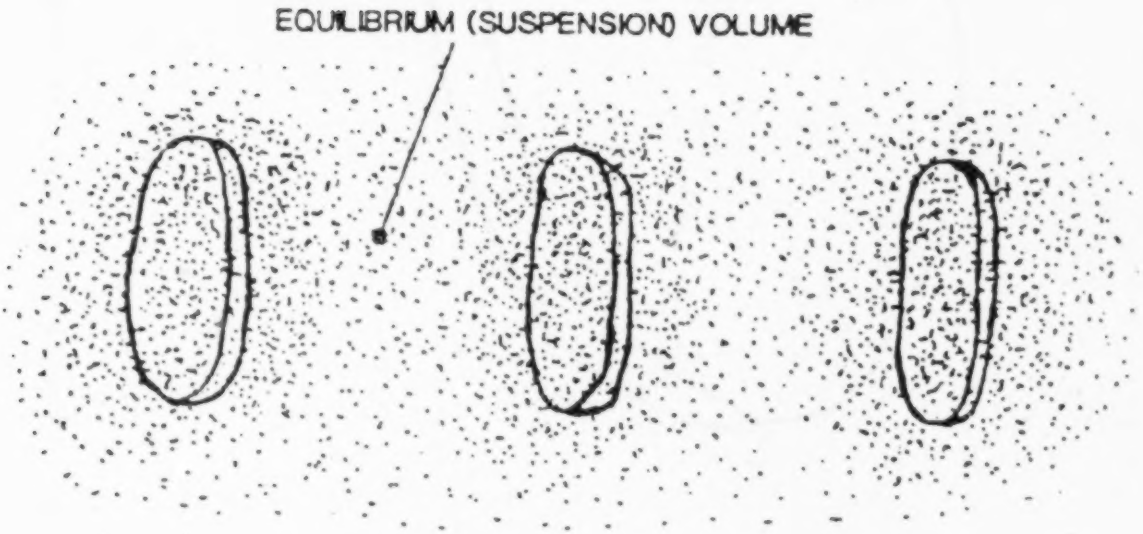


Fig. 5. Particle interaction and equilibrium suspension volumes.

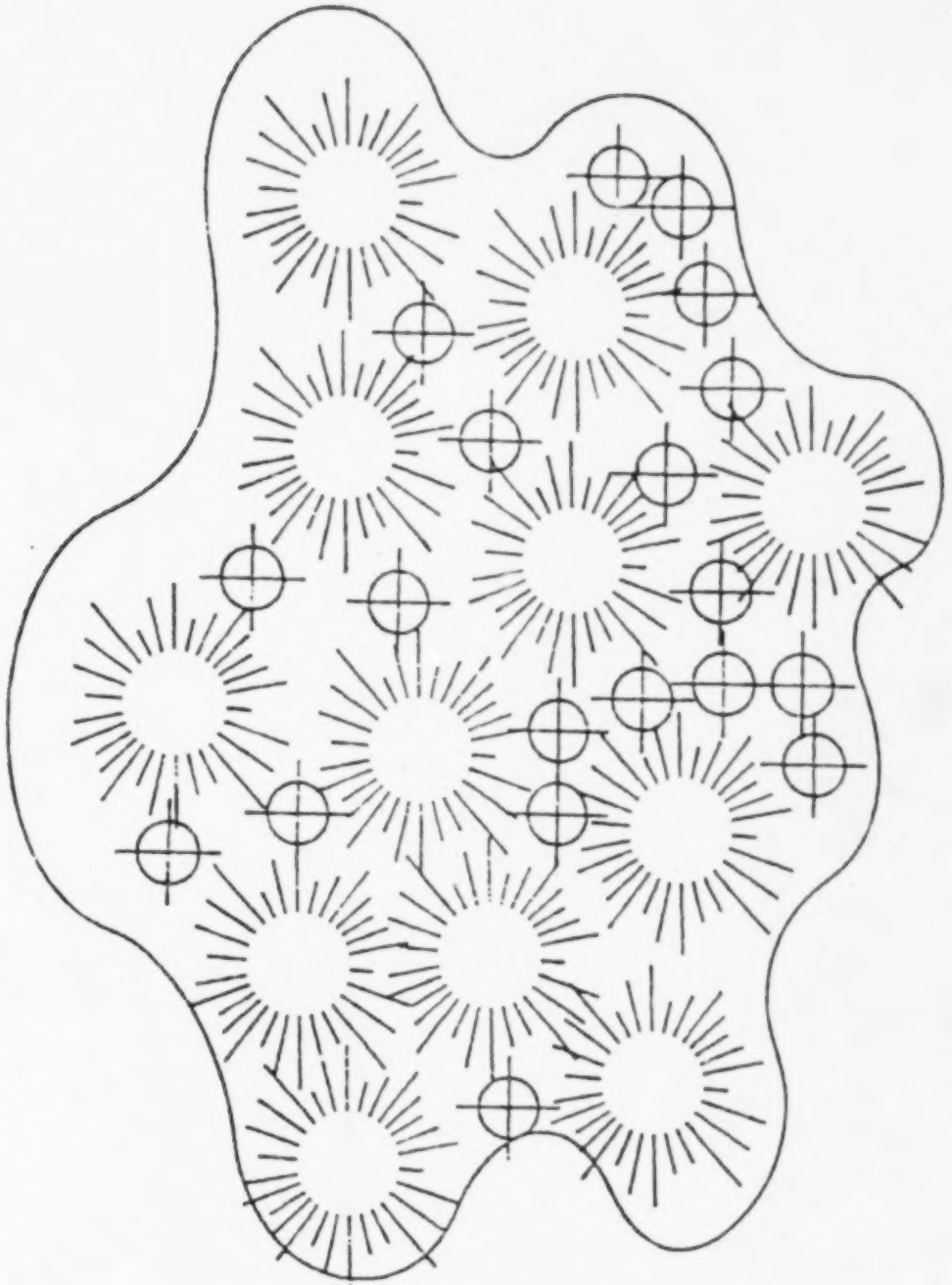


Fig. 6. Overall addition of specific constituent suspensions volumes.